1.0

1.1

1.25   1.4   1.6

4.5
5.0
2.5

2.8   2.5

3.2   2.2

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Radiative Transitions for Molecular Collisions in an Intense Laser Field*

By Thomas F. George,† Jian-Min Yuan,
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Quantum mechanical and semiclassical approaches are discussed for the study of molecular collisions in an intense laser field. Both a coherent state and Fock state representation of the photon field are investigated. The collision dynamics is described in terms of transitions between two electronic-field potential energy surfaces, where each surface depends on the field-free adiabatic surfaces and electric dipole transition matrix elements as functions of nuclear coordinates. The electronic-field surfaces exhibit avoided crossings (on the real axis) due to the radiative coupling at the resonance nuclear configurations, and other parts of these surfaces are similar to the field-free adiabatic surfaces with one of them shifted by $\hbar\omega$ for single photon processes. Metastable states, formed at some collision energies, are conjectured to occur in the field, although absent from the field-free case. From a spectroscopic point of view, changes in energy spectra are expected from those of the individual collision-free species. Numerical results are presented for the collinear collision process $Br(^2P_{3/2}) + H_2(v = 0) + \hbar\omega \rightarrow Br(^2P_{1/2}) + H_2(v = 0)$.

1. INTRODUCTION

There are recent experimental studies on the enhancement of electronically inelastic collision cross sections due to intense optical radiation[1,2] and on photon absorption spectra due to the intermediate resonant molecular states of collision processes.[3] There has also been recent theoretical effort[4-15] to describe the combined effects of collisional and optical excitations. Some main reasons for the continuation of such effort and the development of new theories to describe the interaction of molecular systems with radiation are the following: (a) a molecular system in the gaseous phase interacting with a radiation field is often better characterized as dynamic rather than static. For example, in ordinary molecular beams a typical collision takes place in about 10^{-13} s, *i.e.*, about the cycle of an infrared laser, in which case a collision and a photon absorption should not be viewed as separate processes, particularly when absorption takes place in an intense laser field; (b) for intense field strengths and/or multiphoton processes, time-dependent perturbation theory is not valid; (c) the effect of the interaction with a quantized field as well as a classical field should be investigated for molecular systems.

In this paper we are interested in atom-atom and atom-diatom collision processes in the presence of an intense laser field. In order to maintain a clear and simple physical picture, we shall focus on single photon processes for a two-(electronic) state molecular system in a single mode laser, although our formal presentation can be extended readily to more general cases.[15,16] A related, interesting work is that of

Kroll and Watson[7] which deals with single- and multi-photon processes for a two-level collision system in a single field mode, using a number representation for photon states. This theory has been extended by Lau[12] to a multi-level system interacting with single and multi-field modes. While these treatments are indeed interesting, they are perhaps a bit too complicated to give a simple physical picture. On the other hand, their assumption about near-adiabatic scattering is somewhat restrictive for a realistic treatment of atom-diatom collisions.

Within a two-(electronic) state approximation, a semiclassical model[14,15] of molecular scattering in a strong external field has been developed recently in our laboratory, and from this model atom-atom and atom-diatom collision cross sections can be calculated. An analogous quantum mechanical theory[16] has also been derived, and in the next section of this paper we shall outline some of the key results of this theory, where we shall first use a coherent state and then the Fock state as representations of the photon field. We shall also discuss the main feature of the semiclassical model. In the third section we shall present some numerical results from both the semiclassical and quantum mechanical theories for the process

$$Br(^2P_{3/2}) + H_2(v = 0) + \hbar\omega \rightarrow Br(^2P_{1/2}) + H_2(v = 0). \tag{1.1}$$
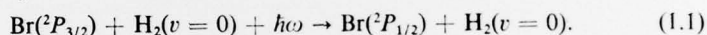
The description of a process such as (1.1) involves the construction of electron-field potential energy surfaces,[17] which depend on the original field-free adiabatic surfaces and electric dipole (or sometimes magnetic dipole and electric quadrupole) transition matrix elements between electronic states as a function of nuclear configurations. It will become evident from our presentation in the next two sections that there is a need for *ab initio* and/or semiempirical studies of radiative transition matrix elements as a function of nuclear configurations as well as studies of field-free surfaces and non-adiabatic coupling.

2. THEORY OF MOLECULAR SCATTERING IN A QUANTIZED FIELD

The time-dependent Schrödinger equation for a molecular collision process in an electromagnetic field is

$$i\hbar\frac{\partial}{\partial t}\Psi(x,q,t) = \mathscr{H}(x,q,t)\Psi(x,q,t), \tag{2.1}$$

where the total Hamiltonian is

$$\mathscr{H}(x,q,t) = T_q + H_{el}(x,q) + H_{rad} + H_{int}(x,q,t), \tag{2.2}$$

and x and q stand for electronic and nuclear coordinates, respectively. The field-free electronic Hamiltonian is given as

$$H_{el}(x,q) = T_x + V(x,q). \tag{2.3}$$

T_q and T_x are the nuclear and electronic kinetic energy operators, respectively, and V is the electrostatic interaction among electrons and nuclei. H_{rad} is the Hamiltonian for the free radiation field of a single cavity mode with frequency ω,

$$H_{rad} = \hbar\omega\hat{a}^\dagger\hat{a}, \tag{2.4}$$

where $\hat{a}$ and $\hat{a}^\dagger$ are the photon annihilation and creation operators. H_{int} is the Hamiltonian for the interaction between the radiation field and the molecular system,

$$H_{int}(x,q,t) = \sum_j e_j Q_j \cdot E_j, \tag{2.5}$$

$$E_j = iE'_0[\hat{a}e^{i(k \cdot Q_j - \omega t - \beta)} - \hat{a}^\dagger e^{-i(k \cdot Q_j - \omega t - \beta)}]. \tag{2.6}$$

where Q_j represents the collective electronic and nuclear coordinates, e_j is the particle charge, E'_0 is related to the strength and polarization of the field, k is the wave vector of magnitude ω/c and the summation is over all particles. The phase β is arbitrary and may be chosen at our convenience. If the wavelength of the field is much longer than the molecular dimension, we can invoke the dipole approximation, namely, to keep only the first term of the power series expansion of $\exp(i k \cdot Q_j)$, so that H_{int} becomes

$$H_{int}(x,q,t) = \mu(x,q) \cdot E(t) \qquad (2.7)$$

where

$$E(t) = i E'_0 [\hat{a} e^{-i(\omega t + \beta)} - \hat{a}^\dagger e^{i(\omega t + \beta)}], \qquad (2.8)$$

and the transition dipole operator μ is defined as

$$\mu = \sum e_j Q_j. \qquad (2.9)$$

The interaction given by eqn (2.7) is of a simpler form than eqn (2.5); however, for molecular systems where the electric dipole transition is very small, higher order transitions such as the orbital part of the magnetic dipole [to get the spin part extra terms related to spin should be added to eqn (2.5)] or electric quadrupole can be considered by including higher terms in the expansion of $\exp(i k \cdot Q_j)$.

The coherent state is often a good representation for a laser field, and since it results in simple expressions for our problem, we shall first consider it for the photon state. The expectation values of H_{rad} and H_{int} in the coherent state α are

$$\langle \alpha | H_{rad} | \alpha \rangle = \alpha^2 \hbar \omega, \qquad (2.10)$$

$$\langle \alpha | H_{int} | \alpha \rangle = E_0 \cdot \sum_j e_j Q_j \cos(k \cdot Q_j - \omega t), \qquad (2.11)$$

where $E_0 = 2\alpha E_0$ and we have chosen real α and $\beta = \pi/2$. With the dipole approximation eqn (2.11) becomes

$$\langle \alpha | H_{int} | \alpha \rangle = \mu \cdot E_0 \cos(\omega t). \qquad (2.12)$$

We can also set $\langle \alpha | H_{rad} | \alpha \rangle$ equal to zero since it is a constant and simply provides an overall energy shift.

To solve eqn (2.1) we expand Ψ in terms of the complete set of real field-free adiabatic electronic wave functions $\varphi_l(x,q)$ as

$$\Psi(x,q,t) = \sum_l a_l(q) e^{-i[E + (l-2)\hbar\omega]t/\hbar} \varphi_l(x,q), \qquad (2.13)$$

where φ_l satisfies

$$H_{el}(x,q)\varphi_l(x,q) = W_l(q)\varphi_l(x,q) \qquad (2.14)$$

with W_l defining a field-free adiabatic potential surface and E the total collision energy (without the field).

By substituting eqn (2.13) into (2.1), multiplying by φ_j and integrating over x, we obtain

$$[E + (j-2)\hbar\omega]a_j e^{-i(j-2)\omega t} = \sum_l e^{-i(l-2)\omega t}\{[(T_q)_{jl} + T_q\delta_{jl} + 2\sum_k (P_k)_{jl} \cdot P_k]a_l(q)$$
$$+ W_l(q)a_l(q)\delta_{jl} + \tfrac{1}{2}\mu_{jl} \cdot E_0(e^{i\omega t} + e^{-i\omega t})a_l(q)\}, \qquad (2.15)$$

where

$$(T_q)_{jl} = \langle \varphi_j | T_q | \varphi_l \rangle \qquad (2.16)$$

$$T_q = -\sum_k P_k^2 \tag{2.17}$$

$$P_k = -i\hbar\nabla_k/\sqrt{2m_k} \tag{2.18}$$

$$(P_k)_{jl} = \langle\varphi_j|P_k|\varphi_l\rangle \tag{2.19}$$

$$\mu_{jl} = \langle\varphi_j|\mu|\varphi_l\rangle. \tag{2.20}$$

For atom-atom systems m_k is the reduced mass and the sum over k is restricted to a single term; for atom-diatom systems the sum is over two terms, one corresponding to the diatom internuclear vector and the other to the vector pointing from the centre of mass of the diatom to the atom. Invoking a two-(electron)state approximation we can reduce eqn (2.15) to

$$[T_q + (T_q)_{JJ} + W_j(q) + (2 - j)\hbar\omega - E]a_j(q) = -e^{-i\omega t}[(T_q)_{jl} + 2\sum_k (P_k)_{jl} \cdot P_k]a_l(q)$$
$$- \tfrac{1}{2}\mu_{jl} \cdot E_0 (1 + e^{-2i\omega t})a_l(q); \quad j,l = 1,2 \text{ and } l \neq j \tag{2.21}$$

where μ_{JJ} has been set to zero for simplicity (this rigorously vanishes in homonuclear atom-atom systems and contributes weakly to electronic transitions in other systems). Making the rotating wave (or resonance) approximation, we drop highly oscillatory terms to obtain in matrix form

$$(\mathbf{H} + \mathbf{Y})a = Ea \tag{2.22}$$

where

$$\mathbf{H} = \begin{pmatrix} T_q + (T_q)_{11} & 0 \\ 0 & T_q + (T_q)_{22} \end{pmatrix} \tag{2.23}$$

$$\mathbf{Y} = \begin{pmatrix} W_1(q) + \hbar\omega & \mu_{12} \cdot E_0/2 \\ \mu_{21} \cdot E_0/2 & W_2(q) \end{pmatrix}, \tag{2.24}$$

$$a = \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}. \tag{2.25}$$

Since we are concerned with very large field strengths, the "Rabi precession frequency" $|\mu_{12}| |E_0|/\hbar$ at fixed nuclear configurations can be very large. Therefore the adiabatic surfaces W_1 and W_2 are so strongly coupled through the radiative interaction that the scattering process is most appropriately solved in terms of electronic-field surfaces, which are found through a unitary transformation on $\mathbf{Y}$:[16]

$$(\mathbf{F}^{\dagger} \mathbf{H} \mathbf{F} + \mathbf{E})f = Ef \tag{2.26}$$

where

$$\mathbf{E} = \mathbf{F}^{\dagger} \mathbf{Y} \mathbf{F} = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} \tag{2.27}$$

$$f = \mathbf{F}^{\dagger} a \tag{2.28}$$

$$\mathbf{F} = \frac{1}{2R}\begin{pmatrix} [\Delta + S] & \mu_{12} \cdot E_0 \\ -\mu_{12} \cdot E_0 & [\Delta + S] \end{pmatrix} \tag{2.29}$$

$$\Delta = W_2(q) - W_1(q) - \hbar\omega \tag{2.30}$$

$$S = (\Delta^2 + |\mu_{12} \cdot E_0|^2)^{1/2} \tag{2.31}$$

$$R = [S(S + \Delta)/2]^{1/2}. \tag{2.32}$$

The electronic-field surfaces E_1 and E_2 are given as

$$E_j = \tfrac{1}{2}(W_1 + W_2 + \hbar\omega) + \frac{(-1)^j}{2}[(W_2 - W_1 - \hbar\omega)^2 + (\mu_{12}\cdot E_0)(\mu_{21}\cdot E_0)]^{1/2}. \qquad (2.33)$$

Eqn (2.26) is then integrated numerically, where the scattering amplitude (S-matrix) is obtained through appropriate boundary conditions on f. [In practice it may be more efficient to integrate an equivalent equation such as eqn (2.22), in analogy to field-free cases where a diabatic representation is more efficient than the adiabatic representation.][18,19]

Through a path integral approach[14,15] or simply by inspection we can derive a semi-classical approximation to the S-matrix which is the direct semiclassical analogue to eqn (2.26). The semiclassical S-matrix element for the transition from initial state i of reactants to final state f of products is

$$S_{fi} = \Sigma N_{fi} \, e^{iA_{fi}/\hbar} \qquad (2.34)$$

where A_{fi} is calculated in terms of a classical action as

$$A_{fi} = E(t_2 - t_1) + \int_{t_1}^{t_*} dt[T - E_1] + \int_{t_*}^{t_2} dt[T - E_2], \qquad (2.35)$$

$$t_1 \to -\infty, \, t_2 \to \infty.$$

N_{fi} is a normalization factor like that used for field-free collisions,[20–23] T is the classical nuclear kinetic energy and t_* is a time at which the electronic-field surfaces intersect in the complex plane. The summation in eqn (2.34) is over all classical paths which propagate from i to f, switching surfaces at t_* (there can, of course, be more than one t_*).

A close look at eqn (2.22) or (2.26) reveals that field-free nonadiabatic coupling terms, i.e., $(T_q)_{jl} + 2\sum_k (P_k)_{jl}\cdot P_k$, are absent, so that our results are most appropriate for processes which are electronically adiabatic in the absence of the field. Furthermore, our results are restricted to single photon processes due to the use of the rotating wave approximation. Within the context of our discussion so far, a portion of the field-free nonadiabatic coupling can be readily included by means of a vibronic representation which is discussed in the next section. As a more rigorous alternative, we may wish to begin at an earlier stage of the theory to retain the field-free non-adiabatic coupling and to further allow for multiphoton transitions. For this purpose we shall consider the Fock representation of the photon states. Expanding the total wave function in terms of products of Fock states and field-free adiabatic electronic states as

$$\Psi(x,q,t) = \sum_l \sum_n C_{ln}(q)e^{-iE't/\hbar}|\varphi_l\rangle|n\rangle, \qquad (2.36)$$

substituting into eqn (2.1), representing the field as in eqn (2.6) with β again chosen to be $\pi/2$, and multiplying by $\langle m|$ and $\langle\varphi_j|$ we obtain

$$[E' - W_j(q) - m\hbar\omega]C_{jm}(q) = \sum_l [(T_q)_{jl} + \delta_{jl}T_q + 2\sum_k (P_k)_{jl}\cdot P_k]C_{lm}(q)$$
$$+ \sum_l \{\mu_{jl}\cdot E'_0[\sqrt{m+1} \, e^{i\omega t}C_{l(m+1)}(q)$$
$$+ \sqrt{m} \, e^{i\omega t}C_{l(m-1)}(q)]\}. \qquad (2.37)$$

Defining B_{lm} through the equation

$$C_{lm} = B_{lm} \, e^{im\omega t}$$

we can rewrite eqn (2.37) as

$$[E' - W_j(q) - m\hbar\omega]B_{jm}(q) = \sum_l [(T_q)_{jl} + \delta_{jl}T_q + 2\sum_k (P_k)_{jl} \cdot P_k]B_{lm}(q)$$
$$+ \sum_l \{\mu_{jl} \cdot E'_0[\sqrt{m+1}\, B_{l(m+1)}(q) + \sqrt{m}\, B_{l(m-1)}(q)]\}.$$

$$(2.38)$$

While in principle we can solve eqn (2.38) directly, in practice we can make it more tractable by introducing a two-state approximation whereby the coupling between the levels $(1, m_0 + 1)$ and $(2, m_0)$ is significantly larger than either of the two with a third level [in the level notation $(2, m_0)$, 2 represents the upper electronic state and m_0 is the photon number, etc.] With this approximation we again restrict ourselves to single photon processes. Setting $E = E' - m_0\hbar\omega$ and $\mu_{ll} = 0$, we then have the following two coupled differential equations which contain field-free nonadiabatic coupling:

$$[H_{11} + W_1(q) + \hbar\omega - E]B_{1(m_0+1)}(q) = [(T_q)_{12} + 2\sum_k (P_k)_{12} \cdot P_k]B_{2(m_0+1)}(q)$$
$$+ \mu_{12} \cdot E'_0[\sqrt{m_0 + 2}\, B_{2(m_0+2)}(q) + \sqrt{m_0 + 1}\, B_{2m_0}(q)] \quad (2.39a)$$

$$[H_{22} + W_2(q) - E]B_{2m_0}(q) = [(T_q)_{21} + 2\sum_k (P_k)_{21} \cdot P_k]B_{1m_0}(q)$$
$$+ \mu_{21} \cdot E'_0[\sqrt{m_0 + 1}\, B_{1(m_0+1)}(q) + \sqrt{m_0}\, B_{1(m_0-1)}(q)], \quad (2.39b)$$

where H_{il} is a matrix element of $\mathbf{H}$ from eqn (2.23).

Eqn (2.38) and (2.39) are infinite matrix equations and can be solved by iterative methods.[7,12] However, since we are first interested in single-photon processes, we may simplify these equations by limiting the photon indices to just two values, say m_0 and $m_0 + 1$, so that $B_{2(m_0+2)} = B_{1(m_0-1)} = 0$. For an intense field where m_0 is much greater than one, we may assume $B_{1m_0} = B_{1(m_0+1)}$ and $B_{2(m_0+1)} = B_{2m_0}$, in which case

$$(\mathbf{H}' + \mathbf{U}')\,\mathbf{B} = E\mathbf{B} \tag{2.40}$$

where

$$\mathbf{H}' = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \tag{2.41}$$

$$\mathbf{U}' = \begin{pmatrix} W_1 + \hbar\omega & \mu_{12} \cdot E''_0/2 \\ \mu_{21} \cdot E''_0/2 & W_2 \end{pmatrix} \tag{2.42}$$

$$\mathbf{B} = \begin{pmatrix} B_{1(m_0+1)} \\ B_{2m_0} \end{pmatrix} \tag{2.43}$$

$$E''_0 = 2\sqrt{m_0}E'_0 \tag{2.44}$$

$$H_{jl} = (T_q)_{jl} + 2\sum_k (P_k)_{jl} \cdot P_k; \quad l \neq j. \tag{2.45}$$

Eqn (2.22) and (2.40) are similar except that eqn (2.40) has retained the field-free nonadiabatic coupling terms H_{12} and H_{21}. [Eqn (2.40) is still restricted to single-photon processes, and if we are interested in multi-photon (and multi-surface) processes, we must resort to eqn (2.38).] Having thus coupled the surfaces W_1 and W_2 by combined nonadiabatic and radiative interaction terms, we have introduced a resonance approximation in which either kind of coupling can generate transitions between the electronic-field configurations. This point must be kept in mind when interpreting numerical results from eqn (2.40).

3. CALCULATIONS

Sample calculations have been carried out for reaction (1.1) restricted to collinear collisions. The (field-free) electronic degrees of freedom were represented in terms of a 2×2 diatomics-in-molecules matrix as used previously.[24] For this model the interaction of the field with the molecular system was determined from the asymptotic collision species alone, wherein the magnetic dipole term for bromine dominates. Hence, the magnetic component of the laser field appears for E_0 in the previous section. A calculated value of 1.153 atomic units has been reported for the magnetic dipole transition ($^2P_{3/2} \rightarrow {}^2P_{1/2}$) matrix element for a halogen atom,[25,16] and this value was used for μ_{12} (and μ_{21}) appearing in the previous section. A field strength of 5.1×10^6 V cm^{-1} was chosen which corresponds to 10^{-3} atomic units. Since the Br + H$_2$ system displays a resonance behaviour between electronic and vibrational degrees of freedom (in the absence of a field), it was necessary to retain (field-free) vibrational nonadiabatic coupling terms, i.e., $(T_\rho)_{jl} + 2(\boldsymbol{P})_{jl} \cdot \boldsymbol{P}$ where $\boldsymbol{P} = -i\hbar \nabla_\rho / \sqrt{2m_\rho}$ with ρ as the vibrational coordinate. This was done in the quantum calculations using eqn (2.22) — (2.25), where vibronic curves as a function of just the translational coordinate were inserted for W_1 and W_2. These curves were obtained by diagonalizing the electronic Hamiltonian plus the vibrational part of the nuclear kinetic energy operator within a two-(vibronic)state basis as described in ref. (26). The lower curve correlates to Br($^2P_{3/2}$) + H$_2$($v = 0$) while the upper correlates to Br($^2P_{1/2}$) + H$_2$($v = 0$). The two curves are shown schematically as W_1 and W_2 in fig. 1(a).
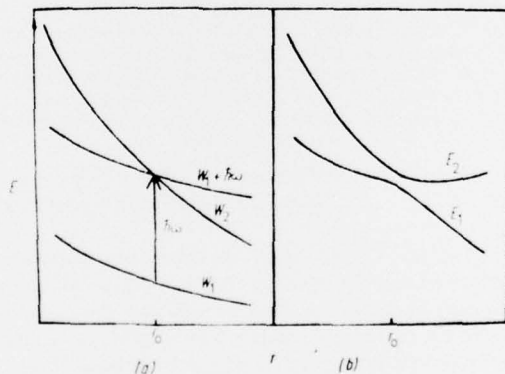

FIG. 1.—(a) Schematic drawing of the two field-free vibronic curves W_1 and W_2 as a function of the translational coordinate r. W_1 correlates to Br($^2P_{3/2}$) + H$_2$($v = 0$) and W_2 correlates to Br($^2P_{3/2}$) + H$_2$($v = 0$). $r_0 = 2.5$ Å is the point at which the field is in resonance with the two curves.
(b) Schematic drawing of the two electronic-field curves E_1 and E_2. Each is a function of W_1, W_2 and the magnetic dipole-field interaction, where this interaction equals the splitting between them at the avoided crossing (r_0).

Solving eqn (2.22) numerically, we obtained the transition probability for reaction (1.1) as a function of the total energy measured relative to the reaction threshold. Results are shown by the solid curve in fig. 2 for the case where $\hbar\omega$ is 1.001 times the asymptotic spin-orbit splitting in bromine. This value of $\hbar\omega$ matches the energy difference between the vibronic curves when bromine is 2.5 Å from the centre of H$_2$. The dotted curve is taken from the field-free-coupled-channel calculations of ref. (24).

Clearly there is an enhanced probability for the process $Br(^2P_{3/2}) + H_2(v = 0) \rightarrow$ $Br(^2P_{1/2}) + H_2(v = 0)$.

Semiclassical calculations were carried out using eqn (2.34) and (2.35), where the two vibronic curves were used for W_1 and W_2 appearing in the expression given by eqn (2.33) resulting in vibronic-field curves E_1 and E_2, which are displayed schematically in fig. 1(b). Analytically continuing these vibronic-field curves to the intersection point in the complex translational coordinate plane, we integrated classical trajectories which switched curves smoothly at this point. The results are shown by the dashed line in fig. 2. In computing these results we used a form for the normalization
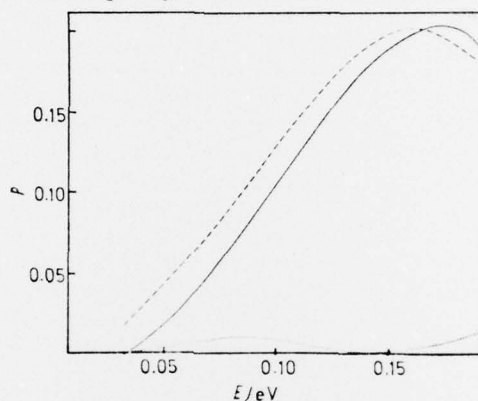

FIG. 2.—Probabilities for the collinear reaction $Br(^2P_{3/2}) + H_2(v = 0) + \hbar\omega \rightarrow Br(^2P_{1/2}) + H_2$ $(v = 0)$ as a function of total energy, measured relative to the reaction threshold. The value of $\hbar\omega$ is 1.001 times the asymptotic spin-orbit splitting. Shown are the results from the quantum calculations using the two-(vibronic)state model (solid line), quantum coupled-channel results with the field turned off (dotted line) and results from semiclassical calculations using the two-(vibronic)-state model (dashed line). The probabilities for the field-free transition (dotted line) have been multiplied by 100.

factor N_{fi} which is analogous to that discussed by Nikitin[26-28] for a purely exponential potential splitting of two diabatic curves (in the field-free case), which is similar to our problem.

There are several obvious shortcomings of the above calculations presented for reaction (1.1), two of which are the restriction to collinear collisions and the neglect of electric dipole transition matrix elements (which can be important when bromine is close to H_2). Inclusion of these elements would generate effects similar to those illustrated in fig. 2 for a field strength considerably smaller than 5.1×10^6 V cm^{-1}. Such shortcomings will be dealt with in future calculations.

4. DISCUSSION

Without carrying out extensive calculations, we can gain insight into how the field can affect a collision process by looking closely at the electronic-field surfaces E_1 and E_2 defined by eqn (2.33). Away from the resonance radiative coupling region of nuclear configurations, E_1 approaches W_2 and E_2 approaches $W_1 + \hbar\omega$ (assuming μ_{12} to be small asymptotically). However, around resonance where $\Delta = W_2 - W_1 - \hbar\omega \approx 0$, there is an avoided crossing due to radiative coupling and E_1 and E_2 become $E_{1,2} = [(W_1 + W_2 + \hbar\omega) \pm |\mu_{12} \cdot E_0|]/2$. Therefore, by shining a radiation field in resonance with $W_2 - W_1$ at some nuclear configuration of the system, we can induce electronic transitions, whether the system is electronically adiabatic or non-

adiabatic in the absence of the field.   Furthermore, the upper electronic-field surface may have a well which can support metastable states (long-lived complexes) at certain collision energies which are absent in the field-free case.   At the same time, there may be a potential barrier arising from the radiative coupling, and this can give rise to special effects such as orbiting resonances.   In the case where μ_{12} is still very large in the asymptotic regions, even more special phenomena may occur which are absent in the field-free case.   From a spectroscopic point of view, it is clear that the radiation coupling effect can result in new absorption or emission spectra which are not expected for the individual (noninteracting) collision species.

Extensive calculations can give us accurate information concerning the above effects as well as collision cross sections and radiative transition probabilities.   However, an important ingredient in these calculations is the electronic transition moments as a function of nuclear coordinates (the electric dipole contribution is usually the only one required, but sometimes the magnetic dipole and/or electric quadrupole contributions will be important) in addition to field-free potential energy surfaces and nonadiabatic coupling.   These moments can be found by *ab initio* and/or semi-empirical techniques.[29-32]

We have assumed the field to be linearly polarized, and in calculations one can find the averaged value of the radiative coupling $\mu_{12} \cdot E_0$ over all orientations.   Polarization effects can also be studied by considering the directional dependence of the radiative coupling, and this will be carried out in future investigations.

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Quantum mechanical and semiclassical approaches are discussed for the study of molecular collisions in an intense laser field. Both a coherent state and Fock state representation of the photon field are investigated. The collision dynamics is described in terms of transitions between two electronic-field potential energy surfaces, where each surface depends on the field-free adiabatic surfaces and electric dipole transition matrix elements as functions of nuclear

20. coordinates. The electronic-field surfaces exhibit avoided crossings (on the real axis) due to the radiative coupling at the resonance nuclear configurations, and other parts of these surfaces are similar to the field-free adiabatic surfaces with one of them shifted by hw for single photon processes, where hw is the photon energy from the external laser. Metastable states, formed at some collision energies, are conjectured to occur in the field, although absent from the field-free case. From a spectroscopic point of view, changes in energy spectra are expected from those of the individual collision-free species. Numerical results are presented for the collinear collision process $Br + H_2(v=0) + hw \rightarrow Br^* + H_2(v=0)$, where Br^* is bromine atom in its upper spin-orbit state.